Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for:

Direct ^{17}O Dynamic Nuclear Polarization of Single-Site Heterogeneous Catalysts

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Experimental and Synthetic Details

SBA-15 type MSN, with a surface area of 672 m^2/g and a 4.4 nm pore diameter, was synthesized according to a modified procedure from the literature.[1] This MSN was then heated to 700 °C under vacuum for 15 h. The sample stored in the glovebox to avoid exposure to ambient water. The MSN (0.500 g) was placed in a Schlenk flask in the glovebox, and then the flask was attached to a Schlenk line (Ar). Excess $H_2{}^{17}O$ (475 µL, 41.1% ^{17}O, purchased from Cortecnet) was added to the MSN material, and the reaction flask was sealed and allowed to react overnight at room temperature. The material was then dried under vacuum for 24 h, and then the ^{17}O-enriched silica was placed in a quartz tube and heated under vacuum at 550 °C for 12 h. The resulting material, ^{17}O-MSN, was transferred to the glove box for storage and further grafting and NMR experiments.

The $Zr(NMe_2)_n$@^{17}O-MSN catalyst was prepared using a modified procedure from the literature.[2] A benzene solution of $Zr(NMe_2)_4$ (0.0480 g, 0.181 mmol, 2.5 mL) was added to ^{17}O-MSN (0.102 g) suspended in benzene (7.5 mL). The suspension was stirred for 20 h at ambient temperature, the mixture was centrifuged, and the supernatant was decanted. Any unreacted $Zr(NMe_2)_4$ was washed from the solid material using benzene (1 × 5 mL) and then pentane (2 × 5 mL). The white solid material was dried under vacuum overnight. This catalyst has been previously characterized by DNP and was shown to be stable towards the solvents and the nitroxide biradicals used in the present study.[2]

To prepare the $Y\{C(SiHMe_2)_3\}_n$@^{17}O-MSN catalyst, a pentane solution of $Y\{C(SiHMe_2)_3\}_3$[3] (0.115 g, 0.175 mmol, 2.5 mL) was added to a suspension of ^{17}O-MSN (0.102 g) in pentane (7.5 mL). The reaction mixture was stirred at room temperature. After 20 h of stirring, the reaction mixture was separated in a centrifuge, and the supernatant was decanted. The unreacted $Y\{C(SiHMe_2)_3\}_3$ was washed from the solid with pentane (3 × 5 mL). The resulting off-white solid material was dried under vacuum overnight. In order to verify that this complex also remained intact under DNP conditions we have acquired a DNP-enhanced ^{13}C spectrum (see Figure S1) using 16 mM TEKPol in dry, deuterated, TCE. The spectrum features 2 resonances at 26 and 0 ppm that can be assigned to the quaternary and methyl carbons of the ligand, respectively. Given that the ligating carbon resonates at -2.92 ppm[4] in the free ligand and 17.3 ppm[3] in the solution-phase complex (the methyl carbons are fairly insensitive) we can conclusively show that the complex has not been hydrolyzed. The additional shift to higher frequency observed here for the quaternary carbon is consistent with the replacement of one of the ligands on the yttrium with a Si-O moiety.

All NMR experiments were performed on a 9.4 T Bruker DNP-MAS system equiped with an AVANCE III console, a 9.7 T gyrotron, and a 3.2-mm low-temperature (100 K) MAS probe. Samples were either impregnated with a 40 mM solution of trityl (Finland trityl, purchased from DyNuPol, see Figure S2a) in $H_2{}^{16}O$ (99.99% ^{16}O, purchased from Aldrich) or a 16 mM solution of TEKPol (purchased from Cortecnet, see Figure S2b) in either protonated or deuterated TCE and were subsequently packed into 3.2-mm saphire rotors. An additional sample of ^{17}O-MSN impregnated with AMUPol in $H_2{}^{16}O$ was also trialed to ensure that the water did not lead to any degradation of the DNP performance in the trityl samples (see Figure S3). For the Y and Zr complexes, the rotors were packed in a glovebox using dry TCE. This preperation approach does not lead to the decomposition of the complexes, *vide supra*. The Finland trityl and

TEKPol biradicals, whose structures are shown in Figure S2, have widths of approximately 1.2 nm and 1.8 nm, respectively, and thus can easily penetrate the 4.4 nm pores of the MSN. For the direct ^{17}O DNP experiments using trityl the magnetic field was increased by 400 ppm from its standard position for ^{1}H DNP using a dinitroxide. Similarly, the magnetic field was decreased by 500 ppm when TEKPol was used as a polarizing agent. Note that the necessary changes in magnetic field, when quoted in ‘ppm’ (as opposed to using frequency or magnetic field units) are independent of the magnetic field, or microwave frequency, of the system used. We suggest that future publications of DNP field sweeps should use these units to facilitate the replication of experiments.

All ^{17}O SSNMR experiments were performed with 12.5 kHz MAS using a spin echo with the excitation and refocusing pulses lasting 10 and 20 μs, respectively. The echo delay was set to a single rotation period. The optimal DFS pulse swept from ±1 MHz to ±250 kHz in 10 ms whereas the optimal HS pulse had a 300 kHz offset, and swept over 12.5 kHz in 10 ms. PRESTO-II, using the $R18_1^7$ recoupling sequence, was used for indirect DNP measurements. Relaxation times were measured using a saturation recovery experiment and the recycling delays were set to ~1.3 T_1 (see Table S1), with the exception of the sample impregnated with AMUPol, for which T_1 was not measured and the recycle delay was set conservatively to 4 s. A total of 64 scans were accumulated for the 'microwave on' direct DNP enhanced spectra of the base silica samples, while a total of 128 scans were accumulated for the 'microwave off' spectra. Those numbers were increased to 1024 and 2048 scans for the 'microwave on' spectra of the Zr and Y complexes, respectively, with a corresponding 5700 and 5600 scans for their 'microwave off' spectra. The intensity of all the spectra shown in the main text were, nevertheless, scaled to reflect the differences in the numbers of scans.

Table S1. Relaxation times and recycle delays used in this study.

material	**polarizing agent**	**T_1 / s**[1]	**t_{rec} / s**
^{17}O-MSN	Finland trityl	1.6	2.1
^{17}O-MSN	TEKPol	2.4	3.1
^{17}O-MSN	TEKPol	1.3[2]	1.8
$Zr(NMe_2)_n$@^{17}O-MSN	TEKPol	8	10
$Y\{C(SiHMe_2)_3\}_n$@^{17}O-MSN	TEKPol	7	10

[1] Note that, as is typical for DNP at 110 K, the build-up times are limited by T_1. The relaxation times were measured with the microwaves on. [2] This corresponds to the values from the indirect DNP experiment.

The ^{13}C DNP-enhanced CPMAS spectrum of the yttrium complex was acquired using a CP contact time of 500 μs, a 2.5 μs ^{1}H excitation pulse and a 2 s recycle delay. A totat of 1024 scans were accumulated.

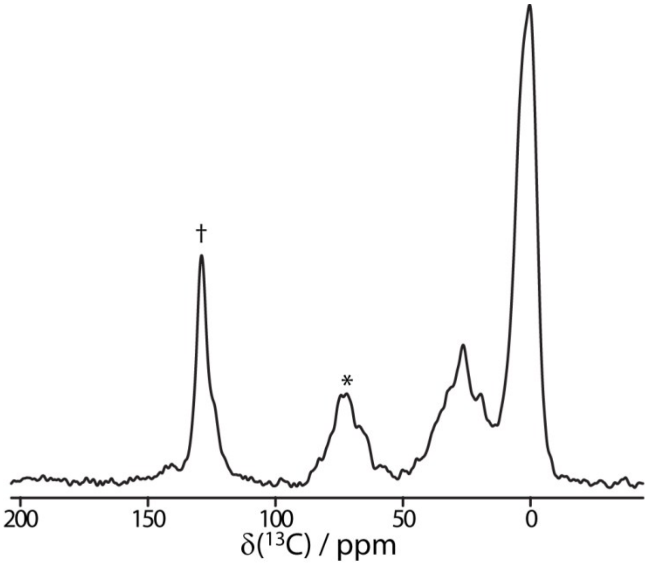
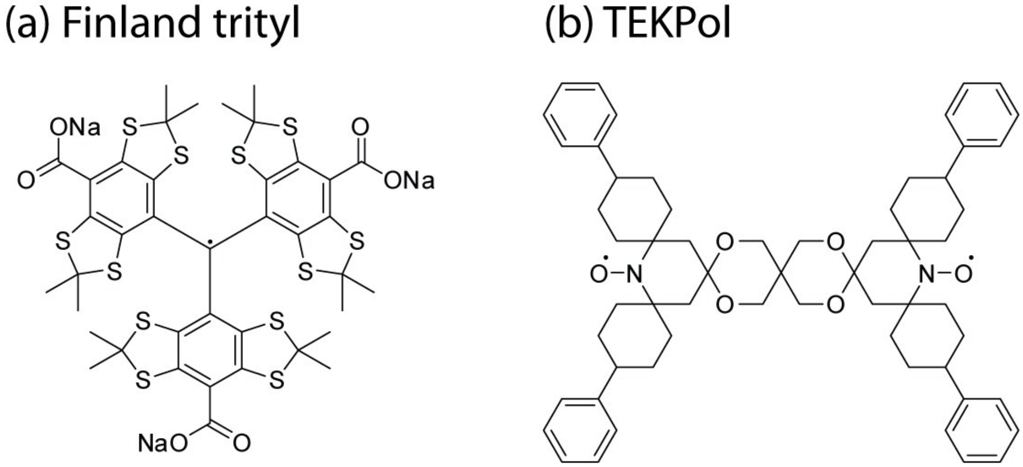


Figure S1. DNP-enhanced ^{13}C CPMAS spectrum of the yttrium complex. An asterisk marks the position of the residual protonated TCE resonance and a dagger marks the resonance from benzene.


(a) Finland trityl

(b) TEKPol

Figure S2. Structures of the Finland trityl (a) and TEKPol (b) polarizing agents.

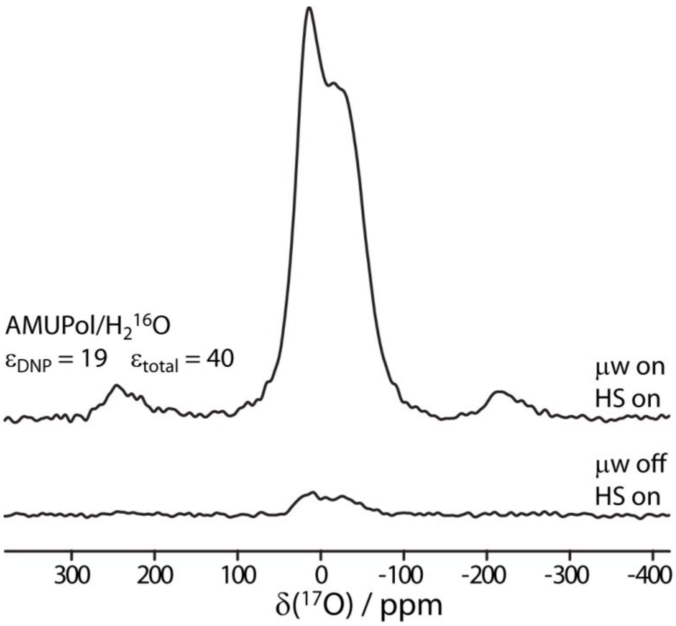


Figure S3. ^{17}O MAS SSNMR spectra of a ^{17}O-MSN sample impregnated with 16 mM solution of AMUPol in $H_2{}^{16}O$. The spectra acquired with the microwaved turned on and off are shown. The enhancement factors are shown on the Figure.

References

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